

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Mechanical Wear of Lightly-loaded Precious Metals

H. C. ANGUS, *Instrum. Prac.*, 1966, 20, (3), 241-246  
A study of the mechanical wear of precious- and base-metal sliding contacts used in miniature brushes and slip rings showed that, of 60 combinations tested, the most wear-resistant incorporate 40% Ag-Pd, Rh, Ir and Ru. The slip ring surfaces were electrodeposited. Both wrought and plated brushes were used.

### Application of Hemispherical Surface Pyrometers to the Measurement of the Emisivity of Platinum (a Low-emissivity Material)

P. R. C. GOARD, *J. Sci. Instrum.*, 1966, 43, (4), 256-258

The total hemispherical emissivity  $E_{ht}$  of Pt was determined with ease using the Land hemispherical surface pyrometer.  $E_{ht}$  varies from 0.078 at 300°C to 0.192 at 1200°C. The spectral hemispherical emissivity  $E_{h\lambda}$  at 0.9  $\mu\text{m}$  for Pt varies from  $0.21 \pm 0.04$  at 900°C to  $0.26 \pm 0.04$  at 1200°C.

### The Magnetic Properties of Platinum Cobalt near the Equiatomic Composition. Part I. The Experimental Data

R. A. McCURRIE and P. GAUNT, *Phil. Mag.*, 1966, 13, (123), 567-577

Magnetisation and crystalline anisotropy measurements on a single crystal 52 at. % Co-Pt disc in the disordered cubic and ordered tetragonal phases show that the easy directions of magnetisation in the cubic phase are  $\langle 111 \rangle$  with anisotropy constant  $\sim -6 \times 10^5$  erg/cm<sup>3</sup> and that the tetragonal phase is uniaxial strongly along [001] with anisotropy constant  $\sim 2 \times 10^7$  erg/cm<sup>3</sup>. Magnetisation loop properties were measured down to 77°K. The coercivity varied linearly with temperature.

### Part II. Mechanism of Magnetic Hardening

P. GAUNT, *Ibid.*, 579-588

Small ordered particles of high anisotropy can pin domain walls and cause the observed hardening. The temperature variation of coercivity is explained by a thermal fluctuation model.

### Magnetic Moments and Unpaired-electron Densities in CoPt<sub>3</sub>

F. MENZINGER and A. PAOLETTI, *Phys. Rev.*, 1966, 143, (2), 365-372

Polarised-neutron studies of ferromagnetic CoPt<sub>3</sub> in various degrees of chemical order showed that the magnetic moments of the components in

fully ordered material are: Co,  $1.64 \pm 0.04 \mu_B$ ; Pt,  $0.26 \pm 0.02 \mu_B$ . Experimental form factors of Pt and Co agree fairly well with theory.

### Antiferro-Ferromagnetic Transition in the Alloys Fe(PtPd)<sub>3</sub>

V. B. KLYUSHIN, I. YA. GETMAN, V. N. ZUBANKOV and V. V. KELAREV, *Fiz. Met. Metalloved.*, 1966, 21, (1), 153-155

FePt<sub>3</sub> and alloys with increasing amounts of Pd up to Fe<sub>25</sub>Pt<sub>40</sub>Pd<sub>35</sub> are antiferromagnetic with the same temperature of magnetic transformation at 170°K. FePd<sub>3</sub> and alloys with amounts of Pd down to Fe<sub>25</sub>Pt<sub>35</sub>Pd<sub>40</sub> are ferromagnetic with Curie point decreasing from 540°K for FePd<sub>3</sub>. The antiferro-ferromagnetic transition occurs between Fe<sub>25</sub>Pt<sub>40</sub>Pd<sub>35</sub> and Fe<sub>25</sub>Pt<sub>35</sub>Pd<sub>40</sub> and its mechanism is discussed.

### Temperature Dependence of the Magnetisation of the Alloy Fe 13.2-Pd 86.8 near the Curie Temperature

G. LONGWORTH, W. L. TROUSDALE, P. P. CRAIG and T. A. KITCHENS, *Bull. Am. Phys. Soc.*, 1966, 11, (2), 237, abs. ED 11

A magnetisation model is proposed in which the local hyperfine field is proportional to the local magnetisation. It leads to a distribution of local magnetisation that becomes unique for  $T/\theta \ll 1$  and to a value of  $\theta$  in agreement with experiment. It yields the average magnetisation from measured hyperfine splitting for  $T/\theta < 0.98$

### Distribution of Magnetisation in the Alloys Fe x - Pd 1 - x

W. L. TROUSDALE, G. LONGWORTH and C. J. SONG, *Ibid.*, abs. ED 12

Fe 13.2-Pd 86.8 at  $0.87 < T/\theta < 0.98$  has temperature dependence of the splitting of the inner pairs of Fe<sup>57</sup> Mössbauer spectral lines which obeys  $M/M_s = A[1 - (T/\theta)^\beta]$  with  $\beta = 0.44 \pm 0.02$ ,  $A = 1.21 \pm 0.05$ ,  $\theta = 300.7 \pm 1.0^\circ\text{K}$ .

### The Partial Molar Volume and Solubility of Hydrogen in Palladium-Silver Alloys

W. T. LINDSAY, *Abs. Papers, 151st Meeting, Am. Chem. Soc.*, 1966, (Mar.), N38

The expansion of four Ag-Pd alloys with up to 40% Ag, during absorption of small amounts of H<sub>2</sub> at 350°C to room temperature and  $p_{H_2}$  from 1 atm to a few mm Hg, and the solubility of H<sub>2</sub> in them were measured. Partial molar volume of H<sub>2</sub> is nearly independent of alloy composition, averaging 1.73 cm<sup>3</sup>/g atom H. Wide variations in expansion during H<sub>2</sub> absorption at constant

temperature are due to solubility effects. Sievert's constants were derived. Heats of solution at infinite dilution correlate with thermal expansion coefficient of the alloys.

### The Low Temperature Transport Properties of the Palladium-Silver Alloy Series

J. S. DUGDALE and A. M. GUENAU, *Phil. Mag.*, 1966, **13**, (123), 503-513

A simple model of the electronic structure of the Ag-Pd system consistent with knowledge of the Fermi surface of pure Pd and the thermodynamic behaviour of the alloys explains the concentration dependence of the resistivity and accounts for the size of the low temperature thermopower in Pd-rich alloys.

### The Relative Heats of Formation of Solid Gold-Palladium Alloys

J. B. DARBY, *Acta Met.*, 1966, **14**, (3), 265-270

Measurements in a liquid-metal solution calorimeter show that the thermodynamic quantity is exothermic over the entire composition range with a maximum at ~40 at.% Pd, as found in the Ag-Pd and Cu-Pd systems. Comparison of the heats of formation of the three systems with other properties indicates that they are partly due to filling the *d* band of Pd with electrons of the noble metals.

### Diffusion of Hydrogen in Copper-Palladium Alloys

J. PIPER, *J. Appl. Phys.*, 1966, **37**, (2), 715-721

At 25°C the diffusion coefficient of H<sub>2</sub> in 0-58 at.% Cu-Pd alloys is relatively insensitive to alloy composition but it increases by two orders of magnitude up to  $5 \times 10^{-6}$  cm<sup>2</sup>/sec during the  $\alpha \rightarrow \beta$  phase change from f.c.c. to b.c.c. Measurements were made of the dependence of the electrical resistivity upon H<sub>2</sub> concentration. At 130°C the increase at this point is due to a decrease in the activation energy for diffusion. Diffusion coefficients of H<sub>2</sub> and D<sub>2</sub> in the b.c.c. alloy have ratio 1.5.

### Unusual Nature of the Abrupt Magnetic Transition in FeRh and its Pseudobinary Variants

J. S. KOUVEL, *J. Appl. Phys.*, 1966, **37**, (3), 1257-1258

When Rh in FeRh was partially replaced by Pd, Pt or Ir, the critical temperature  $T_{crit}$  for first order antiferromagnetic-ferromagnetic transition, which is ~330°K in FeRh, altered. The total entropy change during each transition was deduced.  $\Delta S - \Delta S_{lat}$ , the estimated change in lattice entropy, plotted against  $T_{crit}$  had a maximum at ~500°K just below the Curie point of these alloys. This indicated that  $\Delta S - \Delta S_{lat}$  is an entropy change of magnetic origin caused by thermal excitation of Rh moments which are essentially zero in the antiferromagnetic state.

### Magnetic and Electrical Properties of FeRh Thin Films

J. M. LOMMEL, *Ibid.*, 1483-1484

Magnetisation, coercive force and electrical resistance of thin films of FeRh, prepared by vacuum deposition of alternate layers of Fe and Rh and followed by diffusion annealing, exhibit the phase transition at ~50°C. The transition is broad with large thermal hysteresis. These characteristics are not caused by the clamping of the film to the substrate. Codeposited and sputtered films exhibit little evidence of the transition.

### The Crystal Structure of Rh<sub>2</sub>Te<sub>3</sub>

W. H. ZACHARIASEN, *Acta Cryst.*, 1966, **20**, (3), 334-336

Orthorhombic Rh<sub>2</sub>Te<sub>3</sub> has space group *Amam*, four molecules in the cell and lattice parameters  $a=7.694$ ,  $b=12.446$ ,  $c=3.697$  Å.

### Ordered AB and AB<sub>3</sub> Phases in T<sub>6</sub>-T<sub>9</sub> Alloy Systems and a Modified Mo-Ir Phase Diagram

B. C. GIESSEN, U. JAEHNIGEN and N. J. GRANT, *J. Less-Common Metals*, 1966, **10**, (2), 147-150

The T<sub>6</sub>-T<sub>9</sub> systems of Mo-Rh, Mo-Ir, W-Rh and W-Ir were re-examined to establish whether ordering of the  $\epsilon$  phase exists in the concentration range AB-AB<sub>3</sub>. New phases detected were MoRh, MoIr, WIr, MoRh<sub>3</sub>, MoIr<sub>3</sub>, WRh<sub>3</sub>, WIr<sub>3</sub>. Modifications to the Mo-Ir constitution diagram are proposed.

### Reaction of Tantalum with the Compound NbRu

L. A. PANTALEIMONOV, O. P. NESTEROVA, K. G. AKHMETZANOV, Z. A. GUTS and I. G. SOKOLOVA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1966, (1), 40-42

Studies of the NbRu-Ta system by microscopic and X-ray analysis and determinations of hardness, melting point and electrical conductivity show that minima of the solidus curve and of the electrical conductivity isotherm, maximum hardness and the b.c.c.  $\rightleftharpoons$  tetragonal transition all occur at ~15% Ta-NbRu. The two-phase region between NbRu and Ta, if it exists, is very narrow. 5% Ta-NbRu is rhombic with  $a=4.351 \pm 0.005$ ,  $b=4.253 \pm 0.005$ ,  $c=3.345 \pm 0.005$  Å, nearly identical to NbRu. 14% Ta-NbRu is tetragonal with  $a=3.127 \pm 0.005$ ,  $c=3.328 \pm 0.005$  Å,  $c/a=1.064$  but 15% Ta-NbRu has b.c.c. lattice with  $a=3.286 \pm 0.005$  Å.

### Reaction between the Compounds NbRu and TaRu

L. A. PANTALEIMONOV and O. P. NESTEROVA, *Ibid.*, 43-45

The system NbRu-TaRu, which was studied by microscopic and X-ray analysis and by determinations of hardness, melting points and electrical conductivity, consists of a continuous

series of solid solutions with a solidus ranging from 2050°C for TaRu to 1900°C for NbRu. Maximum hardness and minimum electrical conductivity and temperature coefficient of electrical resistivity all occur at 50 mol. % TaRu.

#### The Crystal Structure of $Ru_4Al_{13}$

L.-E. EDHAMMAR, *Acta. Chem. Scand.*, 1965, **19**, (9), 2124-2130

$Ru_4Al_{13}$  has lattice parameters  $a=15.86$ ,  $b=8.188$ ,  $c=12.74\text{\AA}$ ,  $\beta=107.8^\circ$  and is isotypical with  $Fe_4Al_{13}$  but not with  $Os_4Al_{13}$ .

#### Evaluation of Chromium-Ruthenium Alloys

C. S. WUKUSICK, *U.S.A.E.C. Rept. GEMP-362*, 1965, 25pp

Ru and Re additions increase the ductility of Cr. Cr-Ru alloys show considerable low temperature twinning and have low ductile-to-brittle transition temperatures in bending. Cracking at low temperature is intergranular. Ru depresses the melting point of Cr, hence the high temperature strength is low; Re has the converse effect.

#### Superconductivity in the Close-packed Intermediate Phases of the V-Ir, Nb-Ir, Nb-Rh, Ta-Rh, Nb-Pt, Ta-Pt and Other Related Systems

V. SADAGOPAN and H. C. GATOS, *Phys. Status Solidi*, 1966, **13**, (2), 423-427

The superconducting behaviour of these systems including Hf-Rh and Hf-Ir, was studied. By considering the  $\sigma$ -phase as close-packed, a smooth relationship was found between its  $T_c$  and those of the other c.p. phases of a given system, and their composition.  $\sigma$ -phase has the highest  $T_c$  in each system. The normal behaviour of the c.p. phases in the pseudobinary systems "NbRu<sub>3</sub>"-NbPt<sub>3</sub>, NbIr<sub>3</sub>-NbPt<sub>3</sub>, "NbOs<sub>3</sub>"-NbPt<sub>3</sub>, ZrPt<sub>3</sub>-NbPt<sub>3</sub> agrees with the Gusman-Brout model.

## CHEMICAL COMPOUNDS

#### Sulphato Complexes of Palladium(II)

R. ESKENAZI, J. RASKOVAN and R. LEVITUS, *J. Inorg. Nucl. Chem.*, 1966, **28**, (2), 521-526

New Pd(II) complexes containing co-ordinated sulphate groups were characterised by infra-red spectra, which show that  $Pd(NH_3)_2SO_4 \cdot H_2O$  has unidentate sulphate groups whereas  $PdSO_4$  and  $[Pd(NH_3)_2SO_4]$  are believed to have polymeric structures with bridging sulphate groups. Chemical and i.r. work suggest that  $[Pd \text{ phen } SO_4]$ ,  $Pd \text{ py}_2SO_4 \cdot H_2O$ ,  $[Pd(DMSO)_2SO_4]$  and  $PdSO_4 \cdot 2H_2O$  involve chelating sulphato groups.

#### On Green Rhodium Sulphate

S. I. GINSBURG, N. N. CHALISOVA and O. N. EVSTAF'eva, *Zh. Neorg. Khim.*, 1966, **11**, (4), 742-750

Green Rh disulphate is formed at 170-180°C by

the reaction of Rh hydroxide with  $H_2SO_4$ . Its structure is discussed.

#### Sulphochlorides and Sulphobromides of Platinum

S. S. BATSANOV, E. D. RUCHKIN and L. A. KHRIPIN, *Izv. Akad. Nauk S.S.S.R., Neorg. Materialy*, 1966, **2**, (1), 105-109

The reaction of S with  $PtCl_2$  and  $PtBr_2$ , studied by thermographic, X-ray and chemical analysis, produces sulphochlorides and sulphobromides with general formula  $PtX_mSn$ , where X is halogen, and m and n depend on the reaction temperature and the quantity of S. The compounds preserve the main structural features of the Pt halides and also appear to be like polysulphide compounds.

#### Study of Gaseous Oxides, Chloride, and Oxychloride of Iridium

W. E. BELL and M. TAGAMI, *J. Phys. Chem.*, 1966, **70**, (3), 640-646

$IrO_3$ ,  $IrCl_3$  and  $IrO_2Cl$  vapour species were formed during the vaporisation of Ir in  $O_2$ ,  $Cl_2$  and their mixtures at 1000-1500°C and were studied by the transpiration method. Enthalpies and entropies of formation were:  $IrO_3(g)$  at 1600°K,  $4.2 \pm 1.0$  kcal/mole and  $-10.5 \pm 2.0$  eu;  $IrCl_3(g)$  at 1500°K,  $24.1 \pm 2.0$  kcal/mole and  $1.3 \pm 2.0$  eu;  $IrO_2Cl(g)$  at 1500°K,  $-1.9 \pm 2.0$  kcal/mole and  $-7.7 \pm 2.0$  eu.

#### The Crystal and Molecular Structure of Tetragonal Ruthenium Dioxide

F. A. COTTON and J. T. MAGUE, *Inorg. Chem.*, 1966, **5**, (2), 317-318

$RuO_2$  has a tetragonal unit cell with  $a=4.491 \pm 0.007\text{\AA}$  and  $c=3.107 \pm 0.005\text{\AA}$ . Ru-O distances are 1.917 and 1.999 Å. Closest O-O contact is 2.52 Å. Closest Ru-Ru distance is 3.107 Å.

## ELECTROCHEMISTRY

#### Hydrogen Oxidation on Platinum

M. P. MAKOWSKI, E. HEITZ and E. YEAGER, *J. Electrochem. Soc.*, 1966, **113**, (2), 204-206

The anodic  $H_2$  reaction on a rotating platinum disc was studied by slow sweep voltammetry (20-95 mV/min) with various electrolytes,  $pH$ , and rotation rates. Numerous curves are plotted for anodic  $H_2$  polarisation, for anodic current density as a function of angular velocity, and for anodic maximum current densities as a function of rotation rate.

#### Investigation of the Adsorption of Carbon Monoxide on Palladium in Aqueous Solutions

A. B. FASMAN, Z. N. NOVIKOVA and D. V. SOKOL'SKII, *Zh. Fiz. Khim.*, 1966, **40**, 556-560

During CO adsorption on a palladised Pd elec-

trode the potential is 100–200 mV, which is almost independent of the medium or of the conditions by which CO is introduced. Temperature has some effect in an acid medium. The medium affects the stability of Pd carbonyl compounds. In alkalis, the latter form only on the electrode surface and have no effect on the charging curve at high temperatures. In acids, stable compounds form which reduce electrode sorption and increase the bonding energy of H<sub>2</sub> sorption.

#### **Electrochemical Syntheses. V. The Direct Synthesis of Methyl Esters of $\alpha$ , $\beta$ -Unsaturated Carboxylic Acids from Some Arylated Olefins and Carbon Monoxide**

T. INOUE and S. TSUTSUMI, *Bull. Chem. Soc. Japan*, 1965, **38**, (12), 2122–2129

Carbomethoxylation of arylated olefins in the presence of a Pt carbonyl compound was carried out by electrolysis of methanolic solutions of the olefins using Pt electrodes. Methyl esters of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids were formed directly as the Pt cathode lost Pt to make the carbonyl. Mechanisms are discussed.

#### **On Some Peculiarities of the Behaviour of Palladium, Ruthenium and Palladium-Ruthenium Electrodes in Solutions of Organic Substances**

V. S. ENTINA, O. A. PETRII and I. V. SHELEPIN, *Elektrokhimiya*, 1966, **2**, (4), 457–464

20–27% Ru-Pd electrodes have high activity for CH<sub>3</sub>OH oxidation. Orders of activity for electro-oxidation of HCOOH and HCOO<sup>-</sup> are Pd ≫ Pt + Ru > Pt > Pd + Ru ≫ Ru and Pd + Ru > Pd > Pt + Ru > Pt > Ru respectively. The effects of mixed Pd-Ru and potentiostatic curves for Ru electrodes are reproduced.

## **ELECTRODEPOSITION AND SURFACE COATINGS**

#### **Physical Properties of Palladium Electrodeposits**

H. C. ANGUS, *Trans. Inst. Metal Finishing*, 1966, **44**, (2), 41–49

Pd electrodeposits produced in electrolytes based on tetrammino-palladous salts were evaluated for appearance, porosity, hardness, stress, ductility and resistance to mechanical wear. Chloride, bromide and sulphate salts of this type give a satisfactory range of coatings which are suitable for use in electrical contacts. Other salts tested were unsuitable.

#### **The Galvanic Production of Crack-free Rhodium Deposits of Increased Thickness**

G. HANSEL, *Metalloberfläche*, 1966, **20**, (2), 67–70  
Crack-free Rh deposits depend on the conditions

of electrolysis, the composition of the electrolyte and on the use of suitable additives. Bright deposits can be obtained in the presence of Cu ions. A Rh electrolyte based on sulphate permits deposits of low internal stress plated at optimum current efficiency. 8  $\mu$ m crack-free deposits have high corrosion resistance despite H<sub>2</sub>S in the atmosphere.

## **CATALYSIS**

#### **Investigations of the Structures of Platinum Films**

I. A. RYZHAK, L. M. KEFELI, B. E. DZEVITSKII and A. V. KHASIN, *Kinetika i Kataliz*, 1966, **7**, (1), 182–184

Electron micrographic and microscopic studies showed that Pt films consist of spongelike conglomerates of Pt crystals. Conglomerates are 1000–2000 Å or more in size; the initial Pt crystals are 100 Å in size. The growth occurs during thermal treatment at 250–400°C but it is delayed by previous O<sub>2</sub> adsorption.

#### **Process Costs. Nitric Acid**

*Chem. Process Engng.*, 1966, **47**, (1), 11–17

Production costs of a wide range of NH<sub>3</sub> oxidation processes are compared. Pt losses are considered for processes operating at various pressures. (26 references).

#### **The Choice of a Nitric Acid Plant**

D. C. OOSTERWIJK, *Trans. Instn. Chem. Eng.*, 1966, **44**, (2), CE38–CE45

This review discusses capital costs, efficiency of processes, Pt losses, maintenance and production of HNO<sub>3</sub>. (6 references).

#### **How Hydrocracking Fits into an All-hydrogen Refinery**

C. H. WATKINS and J. T. FORTMAN, *Oil Gas J.*, 1966, **64**, (11), 102–105

Platforming is used in the production of gasoline in three refinery conformations which vary the hydrocracking procedure to yield maximum quantities of either diesel fuel, jet fuel or gasoline. Processes are described by reference to flowsheets.

#### **Regeneration of Platinum-on-Alumina Catalysts by the Use of Chlorine**

G. N. MASLYANSKII, N. R. BURSIAI, V. I. SHIPIKIN and B. B. KHARKOV, *Khim. i Tekhnol., Topliv i Masel*, 1966, (3), 1–5

Treatment by a mixture of air and 0.4–5.0 vol.% Cl<sub>2</sub> at 350–500°C of poisoned Pt/Al<sub>2</sub>O<sub>3</sub> catalysts increases their activity and improved their selectivity. Cl<sub>2</sub> content of the catalysts increases; metallic impurities such as Fe decrease. Variations in temperature, Cl<sub>2</sub> concentration, rate of Cl<sub>2</sub> supply and duration of treatment do not affect the stability of the catalyst composition nor its

catalytic properties within the limits studied. The cracking capacity is reduced by chlorination at 500°C with less than 0.8–0.9% Cl<sub>2</sub>.

### Studies of Platinum Catalysts for Isomerisation of Paraffin Hydrocarbons

G. N. MASLYANSKII, N. R. BURSIAK and S. A. BARKAN, *Zh. Prikladnoi Khim.*, 1966, **39**, (3), 650–656

Isomerisation by Pt/synthetic Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> depends on the acidity of the catalyst support. Increasing the Na content from 0.09 to 0.80% decreases catalyst activity 9 times. Small amounts of Fe inhibit dehydrogenation but have little effect on isomerisation, e.g. decreasing Pt content from 1.0 to 0.025% reduces activity for isomerisation by only half. This points to isomerisation of paraffin hydrocarbons occurring at the acid centres of the catalyst. Increasing the Al<sub>2</sub>O<sub>3</sub> content of Al<sub>2</sub>O<sub>3</sub> from 8.5–9.0 to 20% increases the stability of the catalyst for isomerisation.

### Effect of Sulphur on the Activity of Platinum Catalysts in the Process of Isomerisation of *n*-Pentane

N. R. BURSIAK and N. K. VOLNUKHINA, *Ibid.*, 656–660

The rate of isomerisation of *n*-pentane on Pt/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> at 40 atm H<sub>2</sub> is reduced 3.6 times as the S content increases from 0.01 to 1.0 wt.%. Isomerisation of olefins on the acid centres of the catalyst support limits the isomerisation of the *n*-pentane on Pt.

### Activation of Platinum Isomerisation Catalysts by Air and by Hydrogen

*Ibid.*, (4), 845–851

On increasing the catalyst treatment temperature in H<sub>2</sub> from 550 to 650°C the isomerisation capacity of Pt/Al<sub>2</sub>O<sub>3</sub> increases. Treating it in air at temperatures between 130 and 500°C increases the isomerisation of *n*-pentane from 15.7 to 41.7% but increasing the moisture content from 0.002 to 0.02 wt.% decreases the rate of isomerisation 1.4 times. As the treatment temperature in H<sub>2</sub> rises from 340 to 500°C, the isomerisation of *n*-pentane increases from 17.8 to 53.2 wt.%. Successive treatments of Pt/Al<sub>2</sub>O<sub>3</sub> in air and H<sub>2</sub> cause an increase in its isomerisation capacity by changing the state of the Al<sub>2</sub>O<sub>3</sub> and forming acid centres on its surface.

### Production of Aromatic Hydrocarbons of C<sub>8</sub> Composition by the Catalytic Reforming of Petroleum Fractions

G. N. MASLYANSKII, S. A. BARKAN and R. F. PANNIKOVA, *Neftekhimiya*, 1966, **6**, (1), 40–46

Aromatic hydrocarbons are produced by reforming petroleum fractions containing 61% paraffins over Pt/Al<sub>2</sub>O<sub>3</sub> at 20–40 atm by dehydrogenation of naphthenes and dehydrocyclisation of paraffins. Reduction of the working pressure assists paraffin aromatisation and selectivity. Cl<sub>2</sub> promotes the

activity and selectivity of Pt/Al<sub>2</sub>O<sub>3</sub> for dehydrocyclisation more than F<sub>2</sub>. Reduction of pressure from 40 to 20 atm and the use of Cl<sub>2</sub>- instead of F<sub>2</sub>-promoted Pt/Al<sub>2</sub>O<sub>3</sub> increases the yield of C<sub>8</sub> compounds by 40%, half by the dehydrocyclisation of paraffins. Xylenes and ethylbenzene are formed.

### Conversions of Dicyclohexyl and Dicyclohexylmethane on Pt- and Pd-Alumina in Catalytic Reforming Conditions

N. I. SHUIKIN and I. I. VOZNESENSKAYA, *Izv. Akad. Nauk. S.S.S.R., Ser. Khim.*, 1966, (2), 348–350

Dehydrogenation occurs during conversions on 0.5% Pt/Al<sub>2</sub>O<sub>3</sub> and on 0.5% Pd/Al<sub>2</sub>O<sub>3</sub> at 450°C, 30 atm H<sub>2</sub>, rate 0.3 h<sup>-1</sup>, H<sub>2</sub>:hydrocarbon=5:1, yielding 79–86% over Pt/Al<sub>2</sub>O<sub>3</sub>, 12–25% over Pd/Al<sub>2</sub>O<sub>3</sub>. Dicyclohexyl dehydrogenation over Pd/Al<sub>2</sub>O<sub>3</sub> occurs more readily than dicyclohexylmethane dehydrogenation. The molecules break at the C–C bonds between the rings. Six-membered rings may be isomerised to five-membered, e.g. methylcyclopentane is formed.

### Butane Adsorption on a Platinum-Alumina Catalyst

W. SCHIRMER and D. GELBIN, *Chem. Tech.*, 1966, **18**, (3), 161–166

Adsorption isotherms and isotheric heats of adsorption of *n*-C<sub>4</sub>H<sub>10</sub> on Pt/Al<sub>2</sub>O<sub>3</sub> agree well with the theory of the energetic heterogeneity of the surface of the catalyst. Kinetic measurements can be explained by a Freundlich equation with constants derived from the theory of surface heterogeneity or from a surface diffusion mechanism. These results give an approximate explanation of the mechanism, which will be revised after further work.

### The First Czechoslovakian Equipment for Reforming Motor Fuel over Pt Catalyst

K. HLINŠTAK, *Ropa Uhlie*, 1965, **7**, (10), 290–295

Pt/SiO<sub>2</sub> catalyst 9060 has been under test for three years in the reforming of Russian crude oil and is to be tested further. After dispersing Pt in the SiO<sub>2</sub> the catalyst was heated to 450°C and reduced in H<sub>2</sub> at 470°C for 4h. Tests determined the octane number and yield of the reformed fuel, the ease of catalyst regeneration and the amount of H<sub>2</sub> produced. The catalyst performed as well as other Comecon catalysts and octane number ~89 was attained.

### Aromatisation of *n*-Hexane at Atmospheric Pressure in the Presence of Platinised Silica Gel Promoted by Sodium

N. R. BURSIAK, S. B. KOGAN and Z. A. DAVYDOVA, *Neftekhimiya*, 1966, **6**, (1), 35–39

Studies of the dehydrocyclisation of *n*-hexane in the presence of Pt/SiO<sub>2</sub> at 545°C, atm. pressure show that the addition of Na to the catalyst causes a sharp increase in its activity for aromatisation.

Optimum concentration of the promoter (0.8 wt.% Na) increases aromatisation of *n*-hexane by 40%. The effect is not solely due to Na affecting the acid centres of the catalyst but can be explained by the effect of Na on the Pt centres.

### The Structure and Activity of Supported Metal Catalysts. I. Crystallite Size and Specific Activity for Benzene Hydrogenation of Platinum/Silica Catalysts

T. A. DORLING and R. L. MOSS, *J. Catalysis*, 1966, 5, (1), 111-115

X-ray data showed that Pt crystallites supported on SiO<sub>2</sub> increased in size during fixing in air up to 800°C. The fine Pt undetectable by X-ray work was also determined. Metal areas derived from crystallite data and allowing for smaller crystallites agree with areas derived from CO chemisorption. Specific activity for C<sub>6</sub>H<sub>6</sub> hydrogenation of catalysts fired below 400°C, which contain various amounts of fine Pt, was constant. Catalysts fired at 400 and 500°C, which contain mostly larger crystallites, had lower specific activity. Those fired at 600 and 800°C were inactive.

### Hydrogen-Deuterium Equilibration and Parahydrogen and Orthodeuterium Conversion over Palladium: Kinetics and Mechanism

J. J. F. SCHOLTEN and J. A. KONVALINKA, *J. Catalysis*, 1966, 5, (1), 1-17

Studies on Pd wires and sponges indicate that two Pd-H phases occur at the surface and affect the kinetics,  $v = Ap^{-0.69} \exp(-12,500/RT)$  molecules cm<sup>-2</sup>sec<sup>-1</sup> over β-PdH. Primary and secondary isotope effects are discussed. A proposed reaction mechanism is related closely to the Rideal mechanism. It accounts for the pressure dependence of the reaction.

### The Magnetic Susceptibility of Dispersed Palladium

H. KUBICKA, *Ibid.*, 39-43

Pd black showed a decrease in paramagnetism with increasing dispersion when compared to massive metal. Magnetic susceptibility of Pd black with 50-450 Å crystallites, surface area 44.0-5.8 m<sup>2</sup>/g was measured at 85-290°K. Results may be due to atomlike electronic states in the highly dispersed Pd.

### Catalytic Exchange of Methane with Deuterium on Palladium-Gold Alloys

D. W. MCKEE, *J. Phys. Chem.*, 1966, 70, (2), 525-530  
CH<sub>4</sub>-D<sub>2</sub> exchange rates for a series of Pd-Au powders at 90-200°C were measured. Stepwise exchange was the dominant mechanism. Specific activity at 100°C showed a small maximum at ~10 at.% Au. The exchange rate decreased with increasing Au content to a negligible value at ~60 at.% Au. Apparent activation energy for

the exchange reaction varied between 14 and 23 kcal/mole with a shallow minimum at ~20 at.% Au.

### Organic Syntheses by means of Noble Metal Compounds. XIV. The Carbonylation of Cyclooctadienes

J. TSUJI, S. HOSAKA, J. KIJU and T. SUSUKI, *Bull. Chem. Soc. Japan*, 1966, 39, (1), 141-145

1,5-Cyclooctadiene-PdCl<sub>2</sub> and CO react in C<sub>2</sub>H<sub>5</sub>OH to form ethyl 4-cyclooctenecarboxylate. Carbonylation of 1,5-cyclooctadiene catalysed by PdCl<sub>2</sub> also gives this, together with cyclooctanedicarboxylate. 1,3-Cyclooctadiene treated similarly gives a low yield of 2-cyclooctenecarboxylate. Pd is the true catalyst and the presence of HCl is essential.

### XV. The Carbonylation of 1,5,9-Cyclododecatriene Catalysed by Palladium

J. TSUJI and T. NOGI, *Ibid.*, 146-149

Carbonylation of 1,5,9-cyclododecatriene in C<sub>2</sub>H<sub>5</sub>OH with PdCl<sub>2</sub> present gives mono- and diesters without ring contraction. No triester is formed. Metallic Pd is the true catalyst and the presence of HCl is also essential.

### XIX. The Hydroformylation Reaction Catalysed by Metallic Palladium

J. TSUJI, N. IWAMOTO and M. MORIKAWA, *Ibid.*, 1965, 38, (12), 2213

PdCl<sub>2</sub> and metallic Pd catalyse the hydroformylation of olefins. Conversion of C<sub>2</sub>H<sub>4</sub> with synthesis gas at 100°C to propionaldehyde is not very great and some C<sub>2</sub>H<sub>6</sub> is hydrogenated to C<sub>2</sub>H<sub>4</sub>. The Pd can be recovered and reused.

### XXII. Palladium-catalysed Carbonylation of Diphenylacetylene

J. TSUJI and T. NOGI, *J. Am. Chem. Soc.*, 1966, 88, (6), 1289-1292

Diphenylacetylene and CO reacted in C<sub>2</sub>H<sub>5</sub>OH in the presence of PdCl<sub>2</sub> and HCl to form α,β-diphenyl-γ-crotonolactone. No carbonylation occurred in C<sub>6</sub>H<sub>6</sub>.

### XXIV. Palladium-catalysed Carbonylation of Propargyl Alcohols and Propargyl Chloride

*Ibid.*, *Tetrahedron Letters*, 1966, (16), 1801-1804  
Carbonylation of propargyl alcohol in CH<sub>3</sub>OH containing HCl in the presence of Pd/C at 100°C and 100 kg/cm<sup>2</sup> CO yielded methyl itaconate and small quantities of other compounds. Substituted propargyl alcohols reacted similarly. Carbonylation of propargyl chloride in CH<sub>3</sub>OH in the presence of PdCl<sub>2</sub> at 100 kg/cm<sup>2</sup> CO yielded methyl itaconate again. The method is useful for synthesis of alkylidene succinates.

### Oxidation of Butene-1 by Palladous Chloride in Acetic Acid

A. P. BELOV and I. I. MOISEEV, *Izv. Akad. Nauk. S.S.S.R., Ser. Khim.*, 1966, (1), 139-141

Oxidation of butene-1 in the presence of PdCl<sub>2</sub> in glacial CH<sub>3</sub>COOH forms a mixture of the

following alkenyl esters: acetates of buten-1-ol-3, buten-1-ol-2, *trans*- and *cis*-buten-2-ol-2, *trans*- and *cis*-buten-2-ol-1.

### Isomerisation of *n*-Hexane on Molecular Sieves with Y Structure, Containing Palladium

KH. M. MINACHEV, V. I. GARANIN, L. I. PIGUZOVA and A. S. VITUKHINA, *Ibid.*, 129-133

The amount of isomerisation of *n*-hexane on 0.5% Pd/synthetic zeolite depends on the ratio of  $\text{SiO}_2:\text{Al}_2\text{O}_3$  in the type Y zeolite. When  $\text{SiO}_2:\text{Al}_2\text{O}_3=4.5$ , equilibrium is approached at 88% with respect to all isomers (70.3 mol.%) and at 55% with respect to 2,2-dimethylbutane (11 mol.%).

### Catalytic Oxidation of Methane

R. MEXAKI and C. C. WATSON, *Ind. Engng. Chem., Process Design Dev.*, 1966, 5, (1), 62-65

A flow-type integral reactor was used in tests on the oxidation of  $\text{CH}_4$  over Pd/ $\text{Al}_2\text{O}_3$  at 320-380°C, 1 atm. The reaction rate was controlled by a surface reaction in which gaseous  $\text{CH}_4$  reacted with adsorbed  $\text{O}_2$  to form adsorbed  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

### The Hydrogenation of Acetylene. II. The Reaction of Acetylene with Hydrogen Catalysed by Alumina-supported Palladium

G. C. BOND and P. B. WELLS, *J. Catalysis*, 1966, 5, (1), 65-73

Kinetics and product analyses for  $\text{C}_2\text{H}_2$  hydrogenation catalysed by Pd/ $\text{Al}_2\text{O}_3$  at 0-30°C show four types of behaviour: equimolar mixtures of  $\text{H}_2$  and  $\text{C}_2\text{H}_2$  or  $\text{H}_2$ -deficient mixtures selectively produced  $\text{C}_2\text{H}_4$  with only 2-7%  $\text{C}_2\text{H}_6$ ; reactions with  $\text{H}_2:\text{C}_2\text{H}_2=2:1$  initially selectively produced  $\text{C}_2\text{H}_4$  until all  $\text{C}_2\text{H}_2$  was removed, when  $\text{C}_2\text{H}_6$  formed rapidly; for  $\text{H}_2:\text{C}_2\text{H}_2>2:1$  the reaction became non-selective before complete  $\text{C}_2\text{H}_2$  removal; for initial high  $p_{\text{H}_2}$  the reactions were completely non-selective. In the highly selective region selectivity decreased slightly with increased conversion, increased  $p_{\text{H}_2}$  and decreased  $p_{\text{C}_2\text{H}_2}$ . For high  $\text{H}_2:\text{C}_2\text{H}_2$  ratios added  $\text{C}_2\text{H}_4$  hastened nonselectivity but not at  $\text{H}_2:\text{C}_2\text{H}_2\leq 2:1$ . The  $\text{C}_2\text{H}_2$  hydrogenation mechanism is an extension of that for the Pt-catalysed reaction.

### Reduction of Nitrobenzene and *o*-Nitrophenol on Palladium Polyethyleneterephthalate Catalyst

D. V. SOKOL'SKII, S. F. LANKIN and O. A. TYURENKOVA, *Zh. Fiz. Khim.*, 1966, 40, (3), 732-737

The activity of Pd/polyethyleneterephthalate for reductions of  $\text{C}_6\text{H}_5\text{NO}_2$  and *o*-nitrophenol increases when its temperature of preparation is raised. Reactions are zero order with respect to substrata; first order with respect to catalyst. Reaction products do not poison the catalyst.

Reduction rate decreases with increasing acidity of the medium. Rate of reduction decreases in solution in the order:  $\text{H}_2\text{O}>10\% \text{C}_2\text{H}_5\text{OH}>\text{CH}_3\text{OH}>96\% \text{C}_2\text{H}_5\text{OH}$ . No reaction occurs in dioxane. The rate of hydrogenation is higher for *o*-nitrophenol than for nitrobenzene in analogous conditions.

### Hydrogenation of Dimethylethynylcarbinol on Supported Palladium Catalysts

D. V. SOKOL'SKII and N. A. GOGOL', *Dokl. Akad. Nauk. S.S.S.R.*, 1966, 166, (5), 1140-1142

The activity and specificity of Pd/C, Pd/ $\text{SiO}_2$  and Pd/ $\text{BaSO}_4$  were studied in the hydrogenation of dimethylethynylcarbinol in order to define the mechanism of their use.

### The Preparation of Organosilanols via the Metal-catalysed Reaction of Organosilicon Hydrides with Water

G. H. BARNES and N. E. DAUGHENBAUGH, *J. Org. Chem.*, 1966, 31, (3), 885-887

5% Pd/C, 5% Pd/ $\text{Al}_2\text{O}_3$  and 5% Ru/C catalyse hydrolysis of organosilicon hydrides to organosilanols with good yields and high activity. Other Pt metals on C or  $\text{Al}_2\text{O}_3$  are also active. This method applies to silanols sensitive to condensation and to those containing siloxane linkages without cleavage or linkage rearrangement.

### Selective Reduction of Aliphatic Functional Nitro-compounds

S. L. IOFFE, V. A. TARTAKOVSKII and S. S. NOVIKOV, *Uspekhi Khim.*, 1966, 35, (1), 43-69

Catalysts mentioned in this review include Ni/Re,  $\text{PtO}_2$ , 5% Pd/ $\text{BaSO}_4$ , Raney Ni, 5% Pd/C, Fe and Zn. (156 references).

### Catalytic Activity of Platinum Group Metals for the Decomposition of Hydrogen Peroxide

N. I. STROGANOVA, S. A. KHASSAN, G. I. EMEL'YANOVA and V. P. LEBEDEV, *Zh. Fiz. Khim.*, 1966, 40, (2), 475-477

Catalytic activity of Rh and Ir blacks for  $\text{H}_2\text{O}_2$  decomposition was studied. Absolute catalytic activity of Rh, Pd, Ir and Pt was compared. A compensation effect occurs with inversion point at 304°K. Activation energy and potential increase with the number of the element in a given period and also between periods 5 and 6.

### The Hydroxide-blacks of Ruthenium and Rhodium as Catalysts for the Hydrogenation of Organic Compounds. I. Their Catalytic Activity and Selectivity in the Hydrogenation of Some Aromatic Compounds

Y. TAKAGI, T. NAITO and S. NISHIMURA, *Bull. Chem. Soc. Japan*, 1965, 38, (12), 2119-2122

Hydroxides of Ru and Rh have good activities for hydrogenations of organic compounds when reduced to the metals in the presence of the

compounds to be hydrogenated. Their activity and selectivity were studied for hydrogenations of aromatic compounds at 85–100°C, high H<sub>2</sub> pressure. Conversions exceeded 75% in all cases. Results are tabulated. Mixed hydroxides give results in line with their compositions. The catalysts are as active as the corresponding oxide catalysts and contain less alkali after preparation.

## II. The Effects of Solvents and Added Alkalis in the Hydrogenation of Aniline

S. NISHIMURA, T. SHU, T. HARA and Y. TAKAGI, *Ibid.*, 1966, **39**, (2), 329–333

The formation of dicyclohexylamine by the hydrogenation of aniline in the presence of hydroxide-blacks of Ru and Rh increased in the order with respect to the solvents: *t*-butyl alcohol  $\approx$  isopropyl alcohol  $\ll$  C<sub>2</sub>H<sub>5</sub>OH  $<$  CH<sub>3</sub>OH and was hindered greatly by small additions of alkali. Addition of NH<sub>3</sub> retarded catalysis by Rh more than by Ru but in the presence of alkali the addition of NH<sub>3</sub> had no inhibitory effect.

## Homogeneous Catalytic Hydrogenation of Aldehydes with Rhodium Carbonyl Catalysts

B. HEIL and L. MARKÓ, *Chem. Ber.*, 1966, **99**, (3), 1086–1088

Aldehydes were hydrogenated to alcohols under hydroformylation conditions at 200°C, 300–350 atm CO + H<sub>2</sub> in the presence of RhCl<sub>3</sub>·3H<sub>2</sub>O, providing that p<sub>CO</sub> is high. The fact that the reaction products are coloured by a dissolved Rh complex implies that Rh carbonyl compounds are the actual catalysts.

## Kinetic Studies of Chloro Complexes of Rhodium as Hydrogenation Catalysts

B. R. JAMES and G. L. REMPEL, *Canad. J. Chem.*, 1966, **44**, (2), 233–242

Anionic [RhCl<sub>4</sub>]<sup>3-</sup>, [Rh(H<sub>2</sub>O)Cl<sub>5</sub>]<sup>2-</sup> and [Rh(H<sub>2</sub>O)Cl<sub>4</sub>]<sup>-</sup> activate H<sub>2</sub> to reduce ferric ion in aqueous acid solution. Activity increased with the number of chloride ligands. Cationic and neutral complexes did not homogeneously catalyse the reduction of ferric ion but were reduced themselves to a powerful Rh heterogeneous catalyst. Chloro complexes of Rh(III) and Rh(I) were ineffective in aqueous solution for homogeneous hydrogenation of the olefinic bond in maleic acid. A dimethylacetamide solution of RhCl<sub>3</sub> effectively catalyses reduction of maleic acid to succinic acid by H<sub>2</sub>.

## Homogeneous Catalysis of D<sub>2</sub>-H<sub>2</sub>O Exchange by Ruthenium(III) Chloride: Evidence for the Heterolytic Splitting of Hydrogen

J. HALPERN and B. R. JAMES, *Ibid.*, (6), 671–675

It was confirmed that in the absence of Fe(III) or other oxidants RuCl<sub>3</sub> homogeneously catalyses D<sub>2</sub>-H<sub>2</sub>O isotope exchange. Kinetic studies indicated that the Ru(III)-catalysed oxidation of D<sub>2</sub> by Fe(III) and the D<sub>2</sub>-H<sub>2</sub>O exchange reaction have related mechanisms with a common

rate-determining step in which D<sub>2</sub> is split heterolytically and a deuteridoruthenium(III) complex is formed.

## FUEL CELLS

### High-performance Hydrocarbon Fuel Cells with Fluoride Electrolytes

E. J. CAIRNS, *Nature*, 1966, **210**, (5032), 161–162  
Porous, Teflon-bonded Pt black electrodes supported on Pt gauze were used in a C<sub>3</sub>H<sub>8</sub>-O<sub>2</sub> fuel cell with Cs<sub>2</sub>CO<sub>3</sub> electrolyte treated with HF. The electrolyte with the best performance (400 mA/cm<sup>2</sup> at 0.2V) was 29.3 mol.% CsF, 60.9 mol.% HF, 9.8 mol.% H<sub>2</sub>O.

### Boron Carbide, a New Substrate for Fuel Cell Electrocatalysts

W. T. GRUBB and D. W. MCKEE, *Ibid.*, 192–194

B<sub>4</sub>C was tested as a support for Pt black. Fuel cell anodes of this type showed enhanced activity of Pt, more resistance to sintering and no adsorption of H<sub>2</sub>, as well as corrosion resistance and stability in oxidising conditions.

## CHEMICAL TECHNOLOGY

### The Effect of Palladium on the Corrosion Resistance of Titanium

N. D. TOMASHOV and YU. M. IVANOV, *Zashchita Met.*, 1966, **2**, (1), 32–37

0.2% Pd added to Ti gives an alloy with improved mechanical properties and corrosion resistance. An increase in Pd content to 0.5% gives no better results. Tests were made on alloys in H<sub>2</sub>SO<sub>4</sub>, HCl and HCOOH. They showed that there is a lower limit of Pd concentration below which passivation of Ti is not observed. This concentration depends on the corrosive nature of the acid. 0.05% Pd is sufficient to somewhat raise the corrosion resistance of Ti in boiling HCOOH and in 10% HCl at 50°C. The effect of Pd in Ti is to reduce the voltage of the cathodic reaction, which displaces the potential of Ti to a more positive value and for larger additions to where Ti is partially or completely passive. Some reduction of the anodic reaction is caused by shielding part of the Ti surface.

## TEMPERATURE MEASUREMENT

### Pressure Dependence of the emf of Thermocouples

R. E. HANNEMAN and H. M. STRONG, *J. Appl. Phys.*, 1966, **37**, (2), 612–614

Contamination, plastic deformation, electrical shunting, and pressure and temperature gradients are evaluated for their contributions to relative and absolute emf corrections to thermocouples

affected by high pressure. A method for obtaining absolute corrections for Pt:10% Rh-Pt and Chromel-Alumel thermocouples for any high-pressure cell is described.

#### Comment on the Pressure Dependence of the e.m.f. of Thermocouples

E. T. PETERS and J. J. RYAN, *Ibid.*, 933

Tests on Pt:13%Rh-Pt, Pt:10%Rh-Pt and Chromel:Alumel are in general agreement with the previous paper at 40 kbar, 200–1000°C but deviations become important if used to extrapolate above 1000°C.

#### A Study of the Thermoelectric Properties of Pt/Ru-Alloys

J. ISRAEL, *J. Nucl. Materials*, 1966, 18, (3), 272–277

The large neutron cross-section of Rh and its transmutation to Pd in nuclear reactors make Rh unsuitable for use in thermocouples in such reactors but Ru has low neutron cross-section and has been tested in Pt:Ru-Pt thermocouples. Oxidising atmospheres must be avoided or volatilisation of Ru occurs. Ru in the alloys tested was analysed by resistivity measurements. Thermo-e.m.f. is a function of Ru content and of temperature. 6% Ru-Pt is the most useful alloy;

working is not difficult and its e.m.f. is almost independent of Ru content. At a given temperature with these alloys e.m.f. does not continue to rise with Ru content.

#### The Derivation of the Provisional Reference Table CCT64, $T=f(W)$ for Platinum Resistance Thermometers for the Range from 12 to 273.15°K. Part I. The Derivation of the Table for the Range from 12 to 95°K

M. PORLOVA, D. I. SHAREVSKAYA, D. N. ASTROV, I. G. KRUTIKOVA, C. R. BARBER and J. G. HAYES, *Metrologia*, 1966, 2, (1), 6–10

#### Part II. The Derivation of the Table for the Range from 90 to 273.15°K

C. R. BARBER and J. G. HAYES, *Ibid.*, 11–13

The provisional reference table CCT 64 was established over the two overlapping subranges. An international comparison of standard Pt resistance thermometers from NBS and PSU (U.S.A.), PRMI (U.S.S.R.) and NPL (U.K.) for the average table took mean values of T after corrections to the individual tables for the range 12–95°K. NPL made readings with an He gas thermometer over the range 90–273.15°K to compare their Pt resistance thermometer with the thermodynamic scale. A skeleton version of CCT 64 is given.

## NEW PATENTS

### METALS AND ALLOYS

#### Ruthenium Alloys

INTERNATIONAL NICKEL LTD.

*British Patent* 1,025,400

Ru alloys of substantial hardness and strength and appreciable ductility are produced by powder metallurgy, comprise Ru dispersed in an Au/Pd matrix and contain 5–35 wt.% Au, 5–35 wt.% Pd, optionally max. 10 wt.% Pt, Rh, Ir, Mo and/or W or their mixtures and the balance Ru, which must amount to at least 60 wt.%.

#### Production of Platinum Metal Articles

THE INTERNATIONAL NICKEL CO. INC.

*U.S. Patent* 3,217,404

Components made of Pt or its alloys with up to 40% Ir, up to 5% Os, up to 50% Pd, up to 40% Rh or up to 15% Ru are united so that the finished structure may be used at up to 1450°C or even higher temperatures, by placing between the parts a brazing alloy comprising 0–100% Au and 0–100% Cu, maintaining the assembly for 0.5–150 min at a temperature at least 100°C above the m.p. of the brazing alloy but below the m.p. of the components and, when the diffusion of Pt into the brazing alloy is complete, raising

the temperature of the assembly above its operational temperature.

#### Palladium Diffusion Tubes

CHEMETRON CORP.

*U.S. Patent* 3,226,915

An improved furnace structure apparatus for the production of high purity H<sub>2</sub> on a commercial scale comprises a number of diffusion cells each of which is equipped with diffusion tubes made of Pd or Pd/Ag alloy.

#### Reaction Tubes Made of or Lined with Platinum

IMPERIAL CHEMICAL INDUSTRIES LTD.

*U.S. Patent* 3,231,625

Fluorochlorobenzenes are made by thermal disproportionation of convenient higher fluorochlorobenzenes in a tube made of or lined with Pt, Ni or C and in the presence of AlF<sub>3</sub> dispersed on MgF<sub>2</sub> and at 700–850°C.

#### Hydrogen Diffusion Tubes

JOHNSON, MATTHEY & CO. LTD.

*Italian Patent* 695,432

H<sub>2</sub> is separated from gaseous mixtures using diffusion tubes formed of Pd or 25% Ag-Pd alloy. This corresponds to *British Patent* 966,122.